PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2001-151937

(43)Date of publication of application : 05.06.2001

(51)Int.Cl.

C08L 3/02
B29C 45/00
C08J 5/18
C08J 9/00
C08J 9/228
C08K 5/053
C08L 97/02
C08L101/16
//(C08L 3/02
C08L101:00
C08L 97:02
C08L 27:12
C08L 33:00)
B29K 1:00
B29L 7:00

(21)Application number : 11-335515

(22)Date of filing : 26.11.1999

(71)Applicant : NIPPON SHOKUHIN KAKO CO LTD

(72)Inventor : HINO JIRO
SHIMOOOSONO TETSUYA
NAKATANI NOBUO

(54) STARCH-BASED BIODEGRADABLE RESIN COMPOSITION AND MOLDED ARTICLE THEREFROM

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a biodegradable composition that maintains a certain level of mechanical properties, offers an improved moldability and is suitable for molding a plant pot that is resilient and has appropriate rigidity and flexibility.

SOLUTION: This composition comprises starch, a starch plasticizer and a fluororesin, or starch, a starch plasticizer, a fluororesin and a biodegradable resin, wherein 0.01-5 pts.wt. of the fluororesin and an 10-50 pts.wt. of the starch plasticizer are used based on 100 pts.wt. of the starch or the total of the starch and the biodegradable resin. An example of the fluororesin is an acrylate- modified fluororesin such as an acrylate-modified polytetrafluoroethylene. The composition is used for producing a molded article such as a shock absorbing filer, a foamed sheet and a foamed molded article.

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[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention uses starch, biodegradability resin, fluororesin, etc. as a principal component, and offers the molding material and Plastic solid in which productivity, biodegradability, and a production cost were more excellent.
[0002]
[Description of the Prior Art] As a starch system biodegradability constituent, the constituent which uses starch as a principal component, and the constituent which compounded starch and biodegradability resin are in use. However, the biodegradation constituent which used starch as the principal component had the problem that mechanical properties (for example, tensile strength (elongation), compressive strength, bending strength, an elastic modulus, an impact resistance value, a degree of hardness, etc.) were insufficient. Furthermore, a fault, like a water resisting property and moisture resistance are inferior was also seen, and use in a large field was difficult.
[0003] Moreover, with the constituent which used starch as some raw materials, fabrication nature in the adhesion in a fluidity or the metal mold in a fabrication machine, the film, and sheet forming in an extruder, such as hanging down (drawdown), had become a problem like the constituent which compounded starch and biodegradability resin. furthermore -- if the blending ratio of coal of biodegradability resin is not made [many] when the starch system biodegradability constituent was made into foam and the constituent which compounded starch and biodegradability resin by a foaming condition's not being uniform or foam tending to become weak is made into foam -- it is -- etc. -- there was also a problem.
[0004] The purpose of this invention is under such a situation to offer the biodegradability constituent which uses the starch holding the mechanical property more than fixed as a principal component. Furthermore, the purpose of this invention is to offer the constituent which compounded the starch by which fabrication nature has been improved, and biodegradability resin. In addition, the purpose of this invention is to offer the foam which a foaming condition becomes from the constituent which has high reinforcement uniformly, and which compounded the biodegradability constituent or starch which uses starch as a principal component, and biodegradability resin.
[0005]
[Means for Solving the Problem] As a result of examination of this invention persons, by blending fluororesin with the constituent which compounded the biodegradability constituent or starch which uses starch as a principal component, and biodegradability resin, it found out that the constituent which canceled the above-mentioned technical problem could be offered, and this invention was completed. This invention consists of the plasticizer for the plasticizer for starch and starch and fluororesin or starch, and starch, fluororesin, and biodegradability resin, and relates to the constituent which contains the plasticizer for starch of the fluororesin of 0.01 - 5 weight section, and 10 - 50 weight section to starch or starch, and the biodegradability resin 100 weight section. Furthermore, the above-mentioned constituent of this invention can contain an impalpable powder waste paper further. Moreover, this

invention can include the Plastic solid which consists of the above-mentioned constituent, and a Plastic solid can be foam.

[0006]

[Embodiment of the Invention] The starch which the constituent of this invention contains can be well-known starch from the former, for example, may be any of raw starch and modified starch. As raw starch, special starch, such as ground starch, such as underground starch, such as potato starch, sweet potato starch, and a tapioca starch, and amylum tritici, corn starch, a sago starch, and amylum oryzae, waxy starch, and high amylose starch, can be mentioned, for example.

[0007] As modified starch, degradation products, such as roast dextrins, such as a white dextrin, a yellow dextrin, and British gum, oxidized starch, and hypoviscosity denaturation starch, and alpha starch can be mentioned. Furthermore, as a starch derivative, the starch ether, such as starch ester, such as acetic ester and phosphoric ester, carboxy ethyl ether, hydroxy ethyl ether, the hydroxypropyl ether, and electropositive starch, can be mentioned.

[0008] If biodegradability resin is carried out, the poly caprolactone which is aliphatic series polyester resin, polylactic acid, a polybutylene horse mackerel peat, polybutylene succinate, a polyhydroxy butyrate BARIRETO copolymer, an acetyl cellulose, polyvinyl alcohol, etc. can be mentioned.

[0009] As fluororesin, the thermoplastics of a fluorine system can be mentioned that what is necessary is just resin which may produce fibrillation in the case of hot forming. As thermoplastics of a fluorine system, polytetrafluoroethylene, fluoride ethylene polypropylene copolymer, a tetrafluoroethylene perphloro alkyl vinyl ether copolymer, tetrafluoroethylene-ethylene copolymer, polychlorotrifluoroethylene resin, polyvinylidene fluoride, etc. can be mentioned, for example. Furthermore, as for fluororesin, it is desirable that it is fluororesin which gave acrylic denaturation from a viewpoint referred to as promoting fibrillation of fluororesin and being easy to acquire the effectiveness of this invention. The fluororesin which gave acrylic denaturation is the mixture of acrylic resin and fluororesin, and acrylic denaturation polytetrafluoroethylene is desirable as acrylic denaturation fluororesin.

[0010] As a plasticizer for starch, it can choose from water and a well-known plasticizer suitably. As a well-known plasticizer, the high-boiling point plasticizer which has biodegradability can be mentioned, for example. As an example of such a plasticizer, ethylene glycol, propylene glycol, a glycerol, a sorbitol, a polyethylene glycol, a polypropylene glycol, 1,3-butanediol, isodecyl alcohol, n-decyl alcohol, a diethylene glycol, diglycerol, polyglycerin, dipropylene glycol, n-octyl alcohol, etc. can be mentioned.

[0011] The loadings of fluororesin are made below into 5 weight sections more than the 0.01 weight sections to the starch 100 weight section or starch, and the biodegradability resin 100 weight section. Although the loadings of fluororesin are suitably determined in consideration of the application of the constituent of this invention etc., unless the foam fields which can demonstrate effectiveness with low loadings are also more than the 0.01 weight sections, the addition effectiveness of fluororesin is not seen. Moreover, if the injection-molding field which needs the total amount of your kind consideration comparatively also exceeds 5 weight sections, effectiveness will be leveling off and will only become cost quantity. The loadings of fluororesin are carrying out to below 1 weight section more than the 0.01 weight sections to the starch 100 weight section or starch, and the biodegradability resin 100 weight section preferably.

[0012] It is appropriate for the loadings of the plasticizer for starch to carry out to below 50 weight sections more than 10 weight sections to the starch 100 weight section or starch, and the biodegradability resin 100 weight section. However, when, as for this rate of a compounding ratio, the ratio and waste paper of starch and biodegradability resin are compounded, the rate of an optimal compounding ratio changes also for that use application with ratios of a waste paper to these complex again. If it is hard to flow and too hard physical properties are shown, when the rates of a compounding ratio of a starch plasticizer are generally under 10 weight sections, and 50 weight sections are exceeded, after will be too soft conversely or making it a product, a possibility that a plasticizer may carry out bleed out arises. The loadings of the plasticizer for starch are below 40 weight sections more than 20

weight sections preferably to the starch 100 weight section or starch, and the biodegradability resin 100 weight section.
[0013] Starch: As for biodegradability resin (weight ratio), it is desirable that it is the range of 100:0-50:50. Since it becomes a principal component, and resin will be classified by plastics and will become in cost and high if the rate of a compounding ratio of starch is less than 50%, it is not desirable.
[0014] In addition to the above-mentioned component, the constituent of this invention can contain a waste paper. By making a waste paper contain, while considering the aesthetic property of paper, there is an advantage that the same physical properties as a molded pulp product can be given. Although waste papers may be any of the collected paper product, an impalpable powder waste paper is preferably used for them. As an impalpable powder waste paper, the fiber length of the direction of a major axis can mention what is 0.2-1mm, for example. By using the waste paper of impalpable powder, the fluidity at the time of molding is improvable. The waste paper of impalpable powder can be manufactured when grinding or polish carries out a waste paper. Moreover, use of the paper powder which an impalpable powder waste paper can mention the paper powder which comes out at the time of polish of bookbinding, and comes out at the time of polish of bookbinding is the most economical. Of course, the usual waste paper can be pulverized and this can also be used as an impalpable powder waste paper.
[0015] Starch or starch, and biodegradability resin: As for an impalpable powder waste paper (weight ratio), it is desirable that it is the range of 80:20-50:50. When creating the sheet which has the aesthetic property of paper like a molded pulp product, it is appropriate to make the weight ratio of a waste paper into 50% or more. However, when the weight ratio of a waste paper exceeds 80%, shaping is extremely difficult and there is an inclination stable operation becomes impossible in **.
[0016] The constituent and Plastic solid of this invention can also contain a well-known additive as occasion demands in the range which does not spoil the physical properties of the ingredient of this invention in addition to the above-mentioned starch, biodegradability resin, an impalpable powder waste paper, and the plasticizer for starch. As such an additive, a stabilizer, an ultraviolet ray absorbent, an antistatic agent, a germicide, an antioxidant, a surfactant, a cross linking agent, lubricant, etc. can be mentioned, for example.
[0017] The constituent of this invention is manufactured by carrying out heating fusion of the raw materials, such as the above-mentioned starch, biodegradability resin, an impalpable powder waste paper, and a plasticizer for starch, and mixing. Heating melting and mixing are 60-220-degree C temperature requirements, and in using an extruder, when using a pressurized kneader dozens of seconds - several minutes, it can be performed by heating for 10 - 60 minutes and mixing. the suitable configuration after carrying out heating fusion and mixing, and the powder of magnitude -- it can be made granular or a pellet type. furthermore, the above-mentioned powder -- the Plastic solid of the shape of a sheet, the pot for seedling raising, etc. can be formed using the constituent of granular or a pellet type. Such a Plastic solid can be acquired by fabricating for example, the above-mentioned constituent by well-known approaches, such as injection molding, extrusion molding, or blow molding.
[0018]
[Example] Hereafter, based on an example, this invention is explained further.
[0019] The example 1 corn-starch (13% of moisture) 100 section, the meta-BUREN A-3000(product made from Mitsubishi rayon, acrylic denaturation polytetrafluoroethylene) 1 section, and the water 30 section were pelletized at 100 degrees C with the extruder for a trial (lab PURASUTO mill made from an Oriental energy machine), after mixing for 10 minutes 1000 rpm with a Henschel mixer (product made from the Mitsui Miike chemically-modified opportunity). This was dried to 13.5% of moisture, and foam was formed at 190 degrees C by the rose-like shock absorbing material manufacturing facility using this pellet.
[0020] The example 2 corn-starch (13% of moisture) 80 section, the diacetyl cellulose (Teijin make) 20 section, the meta-BUREN A-3000 (acrylic denaturation polytetrafluoroethylene made from Mitsubishi rayon) 0.5 section, and the water 40 section were mixed with the Henschel mixer, the obtained mixture was covered over the direct biaxial extruder, and foam was formed at 190 degrees C.
[0021] Only except for meta-BUREN A-3000, foam was formed on the completely same conditions as

an example 1 during the combination presentation of example of comparison 1 example 1.
[0022] Only except for meta-BUREN A-3000, foam was formed on the completely same conditions as an example 2 during the combination presentation of example of comparison 2 example 2.
[0023] The physical-properties test result of rose-like shock absorbing material (foam) is shown in Table 1. Fizz estimated the case where the magnitude of the cellular cel of foam was the almost same magnitude as "homogeneity foaming" from the electron microscope photograph of foam, and it estimated variation as "ununiformity foaming" in the magnitude of a cellular cel (when there are some from which magnitude is different more than twice). With the rheometer by Yamaden Co., Ltd., by rate 10 mm/min, after compression, it eased, it compressed and eased further, and hardness and stability were measured until they became distortion 80% about shock absorbing material (foam) using the wedge-action-die plunger. The diameter of foam measures a diameter with slide calipers, and are ten averages of measured value. Hygroscopicity measured shock absorbing material (foam) from the weight change after preservation for seven days by 20 degrees C and 35%RH. Water absorption floated shock absorbing material (foam) on water, and computed it from the water absorption weight of shock absorbing material (foam) after 24-hour stirring.
[0024]
[Table 1]

	実施例1	実施例2	比較例1	比較例2
発泡性	均一発泡	均一発泡	不均一発泡	不均一発泡
硬さgf／cm²	880	1420	800	810
復元性%	53	45	13	20
発泡体径㎜	15．2	14．7	14．3	14．2
吸湿性 %	0．2	0．15	−0．42	−0．65
吸水率 倍	7．4	8．9	10．1	10．5

[0025] As shown in Table 1, the shock absorbing material (foam) of examples 1 and 2 was excellent in physical properties, such as stability, fizz, hygroscopicity, and a water resisting property, compared with the examples 1 and 2 of a comparison while uniform foaming was obtained. Especially the hygroscopic result shows that the moisture of shock absorbing material does not fall even if it leaves it in low humidity. When it dried in the winter season, moisture evaporated from foam, the equilibrium moisture in foam was lost, consequently the problem of the stable fall by low humidity that flexibility becomes scarce has also suggested not being generated in the Plastic solid (constituent) of this invention. Moreover, compared with there being little torque fluctuation at the time of foam manufacture, and moreover the value having been low in the examples 1 and 2, in the examples 1 and 2 of a comparison, it is intense, and a load is also expensive, and torque fluctuation also had bad productivity. That is, by using the constituent of this invention, there is little torque fluctuation at the time of foam manufacture, and it becomes possible to manufacture the foam of fixed magnitude stably. If torque fluctuation becomes intense to it, the configuration or magnitude of foam will not be fixed and the problem of coloring will also be produced.
[0026] The example 3 corn-starch (13% of moisture) 40 section, the Bionolle #3001 (Showa High Polymer make) 10 section, the impalpable powder waste paper (fiber length of 0.2mm) 50 section, the meta-BUREN A-3000 (product made from Mitsubishi rayon, acrylic denaturation polytetrafluoroethylene) 0.5 section, and the glycerol 40 section were pelletized at 150 degrees C with the extruder for a trial, after mixing for 10 minutes 1000 rpm with a Henschel mixer. Heat softening and heat flow rate kinesis were measured carrying out the temperature up of the obtained pellet with the programming rate of 5 degrees C / min from 50 degrees C under the load of 50kgf using a dice with a diameter [of 1mm], and a die length of 2mm with the flow tester by Shimadzu Corp. Furthermore, the seedling pot was created with the NISSEI PLASTIC INDUSTRIAL injection molding machine (80T) on MAX160 degree C and the conditions of 0.5-1mm of thickness.
[0027] During the combination presentation of example of comparison 3 example 3, only except for meta-BUREN A-3000, the rest created the pellet on the completely same conditions as an example 3,

and obtained the seedling pot using this pellet further.
[0028]
[Table 2]

	実施例3	比較例3
ペレット化	ペレット化可能	ペレット化可能
フローテスター試験		
熱軟化℃	98	98
熱流動化℃	150	150
苗ポット		
離型性	良好	離型し難い
耐水性	良好	水に溶ける
物性	コシが強く、程よい硬さと柔軟性がある	コシがなく脆い

[0029] As shown in Table 2, heat softening in a flow tester trial and heat flow rate kinesis temperature do not change in an example 3 and the example 3 of a comparison. However, when the seedling pot by injection molding was made as an experiment using the constituent of an example 3, with the constituent of the example 3 of a comparison, the problem was in the mold-release characteristic to excelling in a mold-release characteristic. Moreover, a configuration and the mechanical property even of after 24-hour immersion are almost the same as that of immersion before to underwater, and the seedling pot fabricated using the constituent of an example 3 was excellent in the water resisting property. To it, the abbreviation moiety melted into water and, as for the seedling pot fabricated using the constituent of the example 3 of a comparison, the configuration was changing. Furthermore, the seedling pot fabricated using the constituent of an example 3 had strong chewiness, and the seedling pot fabricated to there being hardness and flexibility with a sufficient degree using the constituent of the example 3 of a comparison was limp, and weak.
[0030] After adding the ethylene glycol 40 section and the A-30001.meta-BUREN 4 section to the example 4 corn-starch 100 section and mixing for 10 minutes 1000 rpm with a Henschel mixer, it pelletized at 150 degrees C with the extruder for a trial. This plasticization starch 100 section, Bionolle #1001 After carrying out tumbler mixing of the 100 sections, it applied to the extruder again at 150 degrees C, and plasticization starch and the Bionolle complex constituent were obtained. The sheet of 1mm of thickness was formed with the bottom T-die extruder of a condition of 170 degrees C whenever [stoving temperature] using this constituent.
[0031] Except not blending example of comparison 4 meta-BUREN A-3000, the pellet was created by the same approach as an example 4, and the sheet was formed further.
[0032] The vacuum forming of a seedling pot was tried using the sheet of an example 4 and the example 4 of a comparison. Consequently, when a sheet went into the heating area for vacuum formings in the case of the sheet of the example 4 of a comparison, it was not able to hang down and fabricate downward. To it, in the case of the sheet of an example 4, such a lappet going-down (drawdown) phenomenon was not seen, but was able to obtain beautiful mold goods (seedling pot).
[0033]
[Effect of the Invention] According to this invention, the biodegradability constituent which uses the starch holding the mechanical property more than fixed as a principal component can be offered. Furthermore, according to this invention, the constituent which compounded the starch by which fabrication nature has been improved, and biodegradability resin can be offered. In addition, according to this invention, the foam which a foaming condition becomes from the constituent which has high reinforcement uniformly, and which compounded the biodegradability constituent or starch which uses starch as a principal component, and biodegradability resin can be offered.

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